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LAUNDERING AIDS

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LAUNDERING AIDS

Range of Patent Claim

Laundering aids coated with water soluble coverings, consisting of mixtures of polyvinyl acetal dialkyl amino acetate and one, two or more organic acids which are solid at normal temperatures and which are soluble in an organic solvent. The gram stoichiometric ratio of the latter is 0.4 to 0.9 with respect to the former.

Detailed Description of the Invention

This invention concerns laundering aids. More specifically, it concerns laundering aids coated with substances useful for laundering by means of an [illegible] agent whose solubility varies depending upon the pH. The agent is insoluble in an alkaline laundry liquid, but soluble in a neutral rinsing liquid.

By pre-blending the laundering aids of this invention in the detergent composition or by adding it to the laundry liquid at the same time as the detergent when beginning the laundering process, it is possible to protect the useful substance from the detergent during laundering and to cause it to dissolve in the rinsing liquid as soon as rinsing is begun. This makes possible an effective display of the invented aid's advantages. In addition, since the laundering aids which in the past had to be added during the rinse cycle, are effectively blended or added from the beginning, it is also possible to eliminate the step of adding them.

The laundering process using a washing machine generally consists of the following cycles: water admission, washing, water extraction, rinsing and final water extraction. In the past, the usual practice was for the housewife to select each cycle on the washing machine controls. In such cases there was no inconvenience in adding laundering aids such as softening, bleaching or starching agents during the rinsing cycle. Recently however, as semi-automatic and automatic washing machines have come to be widely used, the housewife has been freed of the necessity of operating the controls during the process. However, since there still remained the work of adding the laundering aids, she was not yet completely freed. In fact, since the process was automatic, it was necessary to pay even closer attention than was necessary in the past so as to add the laundry aids during the rinse cycle.

This is cumbersome to the housewife and also lowers the value of the automatic washing machines. It was hoped that laundering aids or detergents could be developed which would eliminate that difficulty.

In view of the preceding, the purpose of this invention is to provide entirely new laundering aids or detergent compositions which are coated with various types of useful laundering aids. These coatings are insoluble in alkaline laundering liquids but are soluble in the rinse water which has a neutral pH. Since the contents which are automatically dissolved during the rinse cycle will display the aid effects, the housewife is freed from the necessity of adding the laundry aids separately during the laundering process, and the automatic washing machines are able to display their value fully.

The goals of this invention are accomplished by providing laundering aids coated with water soluble coverings consisting of mixtures of polyvinyl acetal dialkyl amino acetate and one, two or more organic acids which are solid at normal temperatures and which are soluble in an organic solvent. The gram stoichiometric ratio of the latter is 0.4 to 0.9 with respect to the former.

The polyvinyl acetal dialkyl amino acetate used in this invention, particularly polyvinyl acetal diethyl amino acetate (herafter abbreviated as AEA), is obtained by partially esterifying the hydrolysate of polyvinyl acetate by means of monochloroacetic acid, acetalizing it with an aliphatic aldehyde having a carbon number of 2-4, and then aminating it with low-grade alkyl amines in which the alkyl parts have a carbon number of 1-4. (Public Disclosure by Sankyo Company, Ltd., in Patent Application Notice 3786-1965) Such substances have the properties of dissolving in water within the acidic region where the pH is less than 5.8. They are used as coatings for preventing moisture absorption by the chemicals and for protecting them from deterioration.

Since the organic acids which are solid at normal temperature and insoluble in an organic solvent, one may mention the following: malic acid, succinic acid, tartaric acid, citric acid, fumaric acid, maleic acid, malonic acid, glutaric acid, adipic acid, phthalic acid, para-toluic acid, naphthalene sulfonic acid, sulfamic acid and para-xylene sulfonic acid. Especially good are dibasic fatty acids such as fumaric acid, malic acid, maleic acid, tartaric acid and adipic acid or mixtures of iso-phthalic acid and para-toluene sulfonic acid.

The coatings of this invention can be manufactured easily, for instance by taking the basic molecular weight of AEA (657) as the standard and by mixing the above-mentioned organic acids with a stoichiometric ratio of 0.4 to 0.9 (gram) in relation to the former in an organic solvent.

If the gram stoichiometric ratio of the above-mentioned organic acid is greater than 0.9, it will be too easily soluble in both the laundry liquid and the rinsing liquid. If it is less than 0.4, on the other hand, it will not dissolve during rinsing at all, and such substances will be unsuitable for use as laundering aids.

In addition, when necessary, plasticizers such as polyethylene glycol, ethylene oxide-propylene oxide copolymers or dibutyl fumerate [?] may be added to the coatings in this invention.

Among the laundering aids covered by the coatings of this invention can be mentioned softening-finishing agents, blueings, fluorescent whitening agents, antifoaming agents, perfumes, starching agents, oxidation or reduction type pleaching agents or [illegible]. These substances are coated after granulation, either singly or in mixtures. Furthermore, in cases where there is reactivity between the coatings and the substances contained in them, the substances contained may be coated in advance with a separate substance and then coated with the invented substance.

In cases where the laundering aids are to be coated with the substance of this invention, the usual procedure is to use a solution which has been dissolved in a suitable low-boiling point solvent. The solvents used in these cases are alcohols

such as methanol, ethanol or isopropanol; or acetone, chloroform, [illegible], methylene chloride, ethylene chloride or ethyl cellosolve; or mixed solvents consisting of these or other solvents containing water.

Next let us list the advantages of detergent compositions of laundering methods applying the laundering aids of this invention.

(1) When the laundering aid is a softening agent:

In the past it was impossible to find any effective softening agents which could be used together with anionic heavy detergents. This was because the softening agents are cationic and have no compatibility with anionic detergents. In order to give them compatibility it would be necessary either to use a special cationic softening agent or to add expensive second substances. However, even when this was done, the softening effect was extremely low, and considerable thermal effects were observed on the laundering properties, which are the properties of the detergent itself. However, when the detergents of this invention are used, the cationic softening agents will be dissolved in the rinsing liquid in which almost all of the anionic detergents have disappeared. There is thus no loss of laundering effect due to the formation of compounds with the anionic detergents. There is also no spotting, and the softening effect can be displayed in full.

(2) When the laundering aid is an antifoaming agent:

Generally speaking, the favorite detergents are those which will foam sufficiently during laundering, but whose foam disappears quickly during rinsing. If an antifoaming agent is added, the foam will be suppressed even during laundering and it was necessary to adjust the amount of antifoaming agent to

be added. However, if the aids pursuant to this invention are used, they will be dissolved during rinsing and the antifoaming effect can be displayed sufficiently with a small amount of the antifoaming agent.

(3) When the laundering aid is a fluorescent dyestuff:

There are some fluorescent dyestuffs which have a remarkably increased dyeing power in neutral or acidic environments as comparied with alkaline environments. If such dyestuffs are blended "as is" in the detergent, one cannot expect an adequate effect because the laundry liquid is alkaline, and they will be removed when the water is drained off. However, if the aids pursuant to this invention are used, they will be dissolved in the neutral rinse water. They can therefore display an adequate effect with the use of a very small quantity.

In the following, this invention is described in detail in terms of test examples and examples of practical applications.

Test Example 1

The coatings were tested in the following way for their solubility.

Para-toluene sulfonic acid was blended with 10 grams of AEA so that the gram stoichiometric ratio would be 0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 and 1.5. This was dissolved in ethanol so that the total amount would be 100 grams. The solutions were poured into a polyethylene sheet and formed into films with a thickness of 0.07 mm ± 0.01 mm by the natural drying method. The films obtained in this way were

shaped to measure 15 mm × 20 mm, and these were used as samples for measuring the solubility.

The solubility was measured by the following method. Tap water or a detergent solution (a 0.17% solution of a heavy detergent sold on the market consisting chiefly of alkyl benzene sulfonic salts, pH 10.2) was placed in a 200 ml beaker. One of the samples prepared previously was added to this solution and stirring was continued under constant conditions by means of a stirrer while keeping the liquid temperature at 20°C ± 1°C. In this way the film was dissolved in the laundering liquid and tap water. The time required for it to dissolve was measured, and this time was used as the solubility of the film tested. The results are as shown in Fig. 1. The solution speed ratio plotted on the ordinate axis in the figure is the ratio between the dissolving time when a film with a gram stoichiometric ratio of 1.0 was dissolved in tap water and the dissolving time of each film.

[Please see next page for Figure 1]

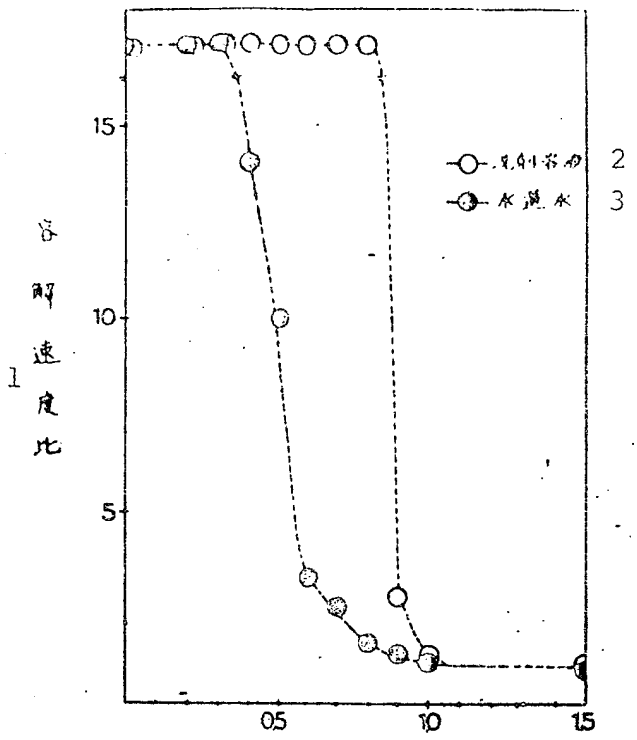

Figure 1: Gram stoichiometric ratio of para-toluene sulfonic acid.

Key: 1. Solution speed ratio
2. Detergent solution
3. Tap water

It is obvious from Fig. 1 that when the organic acid (para-toluene sulfonic acid) has a gram stoichiometric ratio of less than 0.4 with respect to AEA, the solubility is equally poor in both detergent and tap water. It is also clear that the solubility is equally good in both detergent and tap water when the gram stoichiometric ratio is greater than 1.0. On the other hand, when the gram stoichiometric ratio is more than 0.4 and less than 0.9, there is a better solubility in tap water than in detergent.

One may conclude from the facts given above that there is a suitable range for the amount of organic acid to be added to

the coating composition. Although it differs depending on the type of organic acid or depending on the blend of organic acids when two or more are present, one may say that a gram stoichiometric ratio of 0.4 to 0.9 is suitable.

Test Example 2

Solubility tests of the coatings were performed in the following way. 10 parts of AEA and 0.66 parts of tartaric acid were dissolved in ethanol, and the total amount was increased to 100 parts. This solution was poured onto a polyethylene sh-et and films with a thickness of 0.07 mm ± 0.01 mm were formed by the natural drying method. The films obtained in this way were cut to 15mm x 20mm and used as the samples for measuring the solubility.

The solubility tests were performed as follows. Aqueous solutions of various pH were prepared by adding hydrochloric acid or sodium hydroxide to tap water, and the solutions were placed in 200 ml beakers. One of the samples prepared by the method described above was added to this solution, and stirring under constant conditions was continued by means of a stirrer while maintaining the liquid temperature at 20°C ± 1°C. In this way the films would disperse and dissolve in the aqueous solutions of various pH, and the time until they dissolved was measured and used as the solubility of the film tested. The results are shown in Figure 2. The solution speed ratio plotted on the ordinate axis of the graph in this figure is the ratio to the solution time in tap water (pH 6.4). It is obvious from Figure 2 that the coatings used in this invention have a rapidly increasing solubility in the neutral to acid regions.

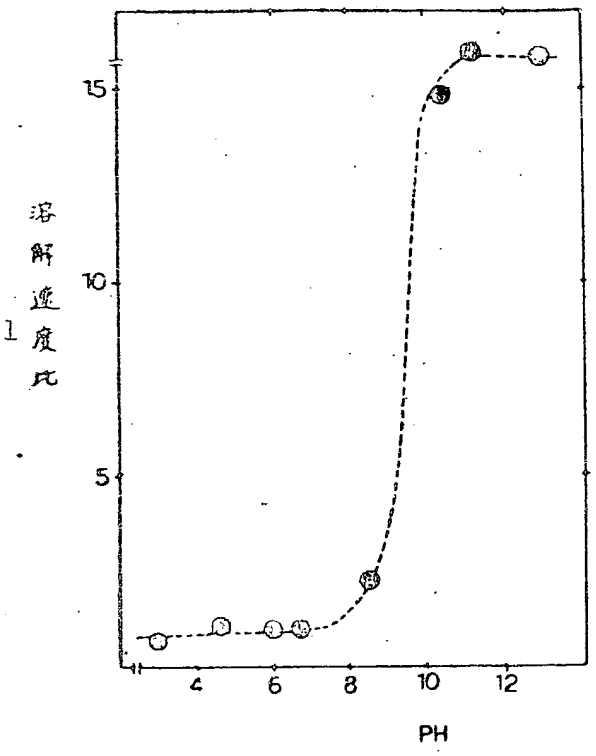

Figure 2: Key: 1. Solution speed ratio

Example 1

Ethanol at approximately 50% by weight is added to a softener composition consisting of 50 parts distearyl dimethyl ammonium chloride and 50 parts sodium bicarbonate. After mixing they are dried and granules are formed. The grain size is adjusted to 24-80 mesh by means of a sieve. The granules are then made into capsules by means of a capsule-making machine. The capsules obtained have a diameter of 12 mm, a thickness of 9 mm and weigh 0.7 grams. These capsules are then coated with a liquid consisting of 10 parts of AEA, 1.54 parts para-toluene sulfonic acid, 0.28 parts of isophthalic acid, and 88.18 parts of ethanol so that it will be 10% by weight converted into terms of the solid contents. Four capsules of the laundering aid obtained in this way and detergent A sold on the mar-

ket (20 parts of straight chain alkyl benzene sulfonic salt, 25 parts of [illegible] salt, 40 parts of Glauber's salt and 15 parts of water) were placed in a washing machine. Clothing (cotton towels and cotton baby towels) was washed for 10 minutes and was rinsed three times.

At the same time, the following tests were also performed in the same way for purposes of comparison.

Comparative Example 1: Only detergent A, sold on the market.

Comparative Example 2: Using a blend made by mixing detergent A sold on the market with 2% by weight of distearyl dimethyl ammonium chloride and 2% by weight of monolauryl trimethyl ammonium chloride as a softening agent.

Comparative Example 3: After washing with detergent A sold on the market, softening agent B sold on the market, the chief component of which is distearyl dimethyl ammonium chloride, was added during the third rinsing in the standard amount used.

Comparative Example 4: When 1.3 mol of an organic acid with respect to AEA was added, a laundering aid coated pursuant to the method described in Example 1 [was added] having the following composition: 10 parts AEA, 2.86 parts paratoluene sulfonic acid and 0.33 parts isophthalic acid.

Comparative Example 5: When 0.2 mol of an organic acid with respect to AEA was added, a laundering aid coated pursuant to the method described in Example 1 [was added] having the following composition: 10 parts AEA, 0.44 parts paratoluene sulfonic acid, 0.04 parts isofumaric acid.

The clothing softening effects were evaluated after these tests, and the results of evaluation are shown in Table 1.

TABLE 1

	Softening effect*
Example 1	1
Comparative Example 1	0
Comparative Example 2	$\frac{1}{?}$ - $\frac{1}{?}$
Comparative Example 3	1
Comparative Example 4	0
Comparative Example 5	0

* The standard for evaluating the softening effect was to take the softening effect when treated with the standard amount of softening agent B sold on the market and when treated with 1/2, 1/? and 1/? of the standard amount. The softness in each case was expressed as 1, 1/?, 1/? or 1/?.

It is obvious from the above Table that, when the product of this invention is used in laundering, it is possible to impart the same softening effect as that observed when a softening agent was added during rinsing, after the completion of laundering.

Furthermore, it is clear from the results of Comparative Examples [illegible] and [illegible] that there is a range of the blending ratio of the organic acid with respect to AEA. If the organic acid has too large a ratio, the coating will dissolve during laundering, as in Comparative Example [?], and it will not be possible to attain the desired effect. On the other hand, when the organic acid has too small a ratio, the coating will remain undissolved even after the rinsing has been completed, as in Comparative Example 5. Here also it will be impossible to attain the desired effect.

Example 2

Capsules of an antifoaming agent composition consisting of [illegible] were prepared and [illegible]. These were [illegible] and [illegible] was measured. For purposes of comparison we also tested for cases where only detergent A sold on the market was used.

TABLE 2

Number of rinsings in Example 3	One
Number of rinsings when only detergent A was used	Three

Brief Explanation of the Figures

Figs. 1 and 2 are graphs showing the [illegible] of the coatings used in this invention.